PB-235 588

# LABORATORY STUDY OF CONTINUOUS ELECTROOXIDATION OF DILUTE CYANIDE WASTES

WATERLOO UNIVERSITY

PREPARED FOR
NATIONAL ENVIRONMENTAL RESEARCH CENTER

OCTOBER 1974

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**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | PB 235 588 |
|---|---|---|
| EPA-670/2-74-059 | | |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| Laboratory Study of Continuous Electrooxidation of Dilute Cyanide Wastes | October 1974; Issuing Date |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| J. J. Byerley and K. Enns | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| Department of Chemical Engineering<br>University of Waterloo<br>Waterloo, Ontario<br>Canada | 1BB036; ROAP 21 AZO, Task 009 |
| | 11. CONTRACT/GRANT NO. |
| | 12010 DOT |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| National Environmental Research Center<br>Office of Research & Development<br>U. S. Environmental Protection Agency<br>Cincinnati, Ohio 45268 | Final |
| | 14. SPONSORING AGENCY CODE |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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An electrochemical demonstration unit has been developed for the treatment of dilute cyanide plating wastes. The cyanide and plating metal concentrations can be reduced to less than 1 ppm. Energy requirements vary according to the duty and mode of operation ranging from 40 KWhr to 140 KWhr/lb $CN^-$.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Industrial wastes<br>Waste water<br>Waste treatment<br>*Metal finishing<br>*Cyanides<br>*Electroplating<br>Industrial waste treatment | Waste water disposal<br>*Chemical wastes<br>Heavy metals<br>Water pollution control<br>*Electrooxidation | 13B |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| Release to public | UNCLASSIFIED | 47 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | UNCLASSIFIED | $3.25-2.25 |

EPA Form 2220-1 (9-7

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U S Department of Commerce
Springfield VA 22151

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EPA-670/2-74-059
October 1974

# LABORATORY STUDY OF CONTINUOUS ELECTROOXIDATION OF DILUTE CYANIDE WASTES

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## FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The studies for this report were undertaken to determine the feasibility of detoxifying dilute cyanide plating wastes by electro-oxidation. This new technology could have a major effect on industry's efforts to protect our Nation's water resources.

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Director
National Environmental
Research Center, Cincinnati

## ABSTRACT

An experimental study was carried out to determine the feasibility of detoxicating dilute cyanide plating wastes by electrooxidation. Because of the toxicity of cyanide to aquatic and animal life and its detrimental effect on the operation of sewage treatment plants, in-plant treatment of dilute cyanide wastes is essential. Although successful processes have been developed for destroying cyanide in concentrated plating wastes, the economic feasibility of electrolytic technique for treating dilute wastes has not been established.

An electrochemical demonstration unit has been developed for the treatment of dilute cyanide plating wastes. The cyanide and plating metal concentrations can be reduced to less than 1 ppm. Energy requirements vary according to the duty and mode of operation ranging from 40 KWhr to 140 KWhr/lb $CN^-$.

This report was submitted in fulfillment of Project Number 12010 DOT, under the partial sponsorship of the U.S. Environmental Protection Agency.

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## SECTION I

## CONCLUSIONS

1. An electrochemical flow reactor/demonstration unit has been developed for the detoxication of dilute (100 ppm range) simple and complex cyanide plating wastes. The cyanide concentration can be reduced to less than 1 ppm.

2. The demonstration unit is also capable of reducing the concentration of plating metals to less than 1 ppm.

3 A standard procedure is illustrated for reactor design based on the operating data of the demonstration unit.

4. Two modes of reactor operation are suggested, the Dragout Duty Mode (DDM) and Total Kill Mode (TKM). Process design is given for independent and combined mode operations.

5. The power cost for operating in the DDM at a 100 ppm level on an 1800 lb $CN^-$ load per year would be approximately $900. The equivalent chemical cost for alkaline chlorination/neutralization treatment of an 1800 lb $CN^-$ load per year would be approximately $3,200.

6. If the treatment system were operated once a week in the TKM on 1200 gallons of 100 ppm $CN^-$ waste with a final effluent of 0.5 ppm $CN^-$, the additional power cost would be approximately $275. per year. Operation in this mode is necessary to prevent undue carbonate blush.

7. Captial cost of equipment to treat 1800 lb $CN^-$ per year is estimated at $8,550. which is approximately 1/2 the cost of a commercial alkaline chlorination installation.

## SECTION II

## RECOMMENDATIONS

It is recommended that in the treatment of cyanide rinse waters that continuous processing be carried out. This method of operation has been described in the report. The attractive feature of this mode of operation is that cyanide can be oxidized at a relatively low unit cost, as well as providing a means of conserving rinse water.

The long term operation of a reactor of the kind described must still be evaluated. Included in this should be an evaluation of electrode erosion, effect of oils, detergents and insolubles on electrooxidation efficiency and the effect of unusually high current densities required from time to time to accommodate surges in the dragout load.

## SECTION III

## INTRODUCTION

The project is directed at solving the pollution problem caused by dilute cyanide wastes from small plating facilities. Generally, it is only in large scale operations where dilute wastes are treated but since collectively huge quantities of dilute cyanide waste effluents are produced daily by a myriad of electroplating and other metallurgical operations, it is essential that in-plant purification processes be developed which are suitable for small scale operations. In many cases, it has not been practical for the small plater to use presently available waste treatment technology. As a result most of the smaller plating plants are discharging directly into sewers and receiving waters with little or no treatment. This project examines the feasibility of electrooxidation as a possible solution to this pollution problem.

The main processes in present use for detoxifying dilute cyanide wastes are chemical. The most widely used is oxidation of cyanide ion by alkaline chlorination using hypochlorites or chlorine. The capital cost of large holding tanks, pumps, filtering, metering, monitoring equipment and space as well as the operating costs can be prohibitively expensive for some small scale operations. Processes of this type produce sludge which generally results in a troublesome disposal problem. Ion exchange appears to be attractive because of its ability to produce a high quality water which can be reused in rinsing operations. This is particularly attractive in areas where water is of high cost. Unfortunately presently available commercial ion exchangers absorb cyanide complexes almost irreversibly thus regeneration of the exchanger resin is not economical. Such processes might be feasible in large scale operations but the economics for small operations requires further study. Other physical methods such as electrodialysis and reverse osmosis have been demonstrated for treating plating rinse waters. On the basis of field information evaporative processes for recovery of plating chemicals and rinse water have found some use.

One of the more promising processes for treating dilute cyanide wastes appears to be electrooxidation. Two approaches are possible, viz., batch operation and continuous processing. The main drawback of batch electrooxidation operations is the capital investment since large electrolysis tanks would be required for treating the effluent from even a small electroplating plant. The main objective of this project was to develop an in-plant continuous electrochemical process for destroying cyanide present in dilute waste by electrooxidation. Electro-oxidation has a number of attractive features:

(a) Cyanide destruction by electrooxidation to the less toxic cyanate or to nitrogen and carbon dioxide would not require the addition of relatively expensive oxidants. Possible secondary contamination of the wastes by overdosage of oxidant is thereby eliminated.

(b) Electrochemical treatment would reduce toxicity due to the transition metals usually present in cyanide wastes through cathodic deposition as well as providing a means of recovering valuable metal values.

(c) Electroplating shops, which produce large volumes of dilute cyanide wastes, have the power sources at hand for electrochemical treatment. Further, since electrochemical operations is a familiar field to platers, no new skills would be required to operate such a process.

(d) The equipment would be relatively simple. The reactor envisaged would consist of vertically stacked carbon electrodes in filter press configuration to permit easy disassembly for cleaning, stripping and electrode replacement.

Previous Investigations

The most pertinent references on the electrochemical treatment of cyanide wastes are discussed below. For convenience of presentation the references have been categorized on the basis of the cyanide concentration in the wastes. For references pertaining to the chemical and physical methods of treating cyanide wastes, the reader is referred to the Progress Report on "A State of the Art Review of Metal Finishing Waste Treatment" submitted to the Metal Finishers Foundation (Nov. 15/68) prepared by Shea et al of Battelle Memorial Institute under F.W.P.C.A. grant No. WPRD 201-01-68.

Electrochemical Treatment of Concentrated Cyanide Wastes: Oyler (1) reported the electrolytic oxidation process for cyanide waste disposal. He worked on the electrolysis of waste copper and zinc cyanide solutions. Copper anodes were used for copper wastes and steel anodes were recommended for treating zinc wastes. The process was carried out at 200°F with vigorous air agitation. In a typical run, a solution containing more than 7 oz/gal. of copper cyanide (15.3g $CN^-$/1) could be reduced to about 0.3 oz/gal. (65.3 mg $CN^-$ per liter) in 5 hours. The following advantages for the process were claimed: (a) little attention is required, (b) metal values are recoverable, and (c) the composition of the solution is not a critical variable. Cotton et al (2) described an electrolytic process for destroying cyanide in spent copper cyanide plating solutions in which copper was plated out on insoluble cathodes and cyanide ion was reduced to less than 1 ppm through anodic oxidation. Sperry and Caldwell (3) electrolyzed spent Rochelle copper strike solutions (data are given on the initial $CN^-$ and $Cu^{++}$ concentrations prior to electrolysis) at 160-200°F using anode current densities between 3.2 and 6.7 amp/$ft^2$. Cathodes and anodes were steel plates. In a typical run, a solution having a cyanide concentration of 3.6 oz/gal. (total $CN^-$) and 2.6 oz/gal. of copper was subjected to an anode current density of 3.3 amp/$ft^2$ at 190-200°F and complete destruction of cyanide

and removal of copper (by cathodic deposition) was accomplished in 21 hours. Because of rapid destruction of the steel electrodes, stainless steel electrodes were suggested. Clevenger and Hall (4) carried out bench scale tests on the use of Acheson graphite as electrodes for the electrolysis of KCN solutions in the presence and absence of KOH or $Ca(OH)_2$. They concluded that the oxidation of cyanide was due principally to the oxygen liberated at the anode from the decomposition of water and that the final reaction in basic solution was the formation of the corresponding alkali carbonates. Equations for the possible anodic reactions were suggested but their validity was not established. Meyer et al (5) electrolyzed 120 g NaCN/l (63.7 g $CN^-$/l) solutions for 4 hours at room temperature using carbon electrodes. With current density ranging from 5-100 amp/$ft^2$, the expected increase in the rate of cyanide consumption with increase in current density was observed, but this was accompanied by decrease in the Faraday efficiency. Adding sodium hydroxide decreased the Faraday efficiency except at 100 amp/$ft^2$. Kurz and Weber (6) reported electrolyzing cyanide solutions at a pH range of 10-12. Sodium chloride was added at a starting concentration of 3% and the $Cl^-$ level was maintained at 80-200 mg/l during the electrolysis. It was claimed that the NaCl solution was electrolyzed into a NaOCl leach during the process and that this leach was responsible for the oxidation of the cyanide ion. Dart et al (7) electrolyzed 90.7 g NaCN/l solutions (48.2 g $CN^-$/l) and spent cyanide plating solutions containing copper, cadmium and zinc. Graphite and platinized titanium anodes were used with current densities up to 80 amp/$ft^2$. The cathode was stainless steel and anode-to-cathode area ratio was 4:1. The rate of destruction of cyanide was directly proportional to the current passed and increased with temperature (range is 50-90°C). The following reactions were reported by the authors:

at the cathode: $2H^+ + 2e = H_2$

at the anode: $2OH^- = 0 + H_2O + 2e$

$CN^- + 0 = CNO^-$

in solution: $CNO^- + 2H_2O = NH_4^+ + CO_3^=$

$CNO^- + NH_4^+ = NH_2\text{-}CO\text{-}NH_2$ (urea)

The same reactions were also proposed by Clevenger and Hall (4). The authors also concluded that the cost of electrical energy for the electrolytic oxidation of cyanide would be about one-third the cost of chlorine for alkaline chlorination of cyanide wastes. Byrne et al (8) described the electrolysis of spent cadmium plating solutions (1.8 - 55.0 g $CN^-$/l). Cadmium was recovered at the cadmium cathode and cyanide was converted to cyanate at the graphite anode. Before the electrolysis, the solution was saturated with salt -- chloride ions being used as

catalyst in the oxidation of cyanide to cyanate. The authors presumed that the role of chloride ion was catalytic; they also considered their system as essentially a commercial chlorine and/or hypochlorite cell. A final treatment with chlorine or hypochlorite reduced the cyanide concentration to less than 1 ppm and hydrolyzed most of the cyanate produced. The following reactions were given for the final treatment:

$$CN^- + Cl_2 + 2OH^- = CNO^- + 2Cl^- + H_2O$$

or $$CN^- + ClO^- = CNO^- + Cl$$

and $$2CNO^- + 3Cl_2 + 4OH^- = 2\ CO_2 + N_2 + 6Cl^- + 2H_2O$$

or $$2CNO^- + 3ClO^- + H_2O = 2CO_2 + N_2 + 3Cl^- + 2OH^-$$

Schmidt and Meinert (9) studied the electrolysis of 10-15% aqueous KCN solutions (40-60 g $CN^-$/l) using platinum electrodes. They found out that the formation of HCN was inhibited in strongly alkaline solutions, i.e., low pH tends to increase the rate of dissipation of cyanide from solution as HCN, and the small amount of gases released at the anode (anode:cathode gases = 1:19) was caused by the anodic discharge of cyanate or hydroxyl ions.

$$2CNO^- + 4OH^- = 2CO_2 + N_2 + 2H_2O + 6e$$

$$4OH^- = O_2 + 2H_2O + 4e$$

Electrochemical Treatment of Dilute Cyanide Wastes: The main processes for treating dilute cyanide wastes are chemical and the most widely used process is the oxidation of cyanide ion by alkaline chlorination using either chlorine or hypochlorites (e.g. NaClO). From the standpoint of detoxifying dilute cyanide, alkaline chlorination is very efficient. However, the cost of capital investment in equipment and controls for this process is relatively high for small scale operations.

One of the more promising processes for detoxifying dilute cyanide wastes appears to be electrooxidation. Laboratory and bench scale studies in batch systems have shown that, in the presence of 3-5 molar excess of chloride ion, cyanide can be electrooxidized with current efficiency as high as 80%. Two studies (7,11) indicate that the cost of electrical power for the anodic oxidation of cyanide ion is about one-third the cost of using NaClO in detoxifying an equivalent amount of cyanide.

Ricks and Trigg (12) reported combined chemical and electrolytic oxidation of spent cyanide solutions at the anode to a few ppm. They employed a hollow porous grahpite anode and air or oxygen was forced through the pores in the electrode. A nickel cathode was used. At an anode current density of 20 amp/$ft^2$ and a temperature of 190°F, cyanide concentration was reduced from 340 to 0.4 ppm in 4 hours. Komendova and Drabeck (13) investigated the combined chemical and anodic oxidation of cyanide ion in the range of 50 mg/1 to 5 g/1. They concluded that the optimum addition of sodium chloride, based on the initial concentration of cyanide, was 3:1 and that a higher addition did not substantially increase the rate of destruction of cyanide or Faraday efficiency. Lur'e and Genkin (14) electrolyzed copper plating wastes batchwise containing 22.7 mg $CN^-$ and 10.5 mg $CNS^-$ per liter between a stainless steel cathode and graphite (or magnetite) anode spaced 50 mm apart. Under continuous aeration, complete removal of $CN^-$ and $CNS^-$ was achieved in 4 hours at 8.7 volts and 0.6 amp/$dm^2$ (5.58 amp/$ft^2$) and in 3 hours at 12 volts and 1 amp/$dm^2$ (9.3 amp/$ft^2$). They also reported that if 3 g of NaCl or 1.5 g of NaCl and 1.5 g of $Na_2CO_3$ were added per liter, the duration of electrolysis lasted 2-2.5 hours at 4.5 volts and 0.6 amp/$dm^2$ (5.58 amp/$ft^2$). The power requirement was 0.4-0.04 KWhr/g $CN^-$. In another work (11), the same authors investigated the electrolytic oxidation of dilute cyanide solutions (15-230 ppm $CN^-$) using a stainless steel cathode and anodes of platinum, graphite, stainless steel, nickel and magnetite. Chloride ions were added as catalyst for cyanide oxidation. The highest current efficiency with the smallest consumption of electrical energy was obtained using a current density of 0.1 amp/$dm^2$ (0.93 amp/$ft^2$) and graphite anodes. The highest current efficiency (82.4%) was reported for a chloride-to-cyanide weight ratio of 5.6. In this run, the cyanide content was reduced from 212 ppm to 2.4 ppm in 3 hours. The authors concluded that the cost of electrical energy for the anodic oxidation of cyanide ion was about 1/3 the cost of using sodium hypochlorite. The following reactions were given:

in solution: $CNO^- + 2H_2O = NH_4^+ + CO_3^=$

at the anode: $CN^- + 2OH^- = CNO^- + H_2O + 2e$

$2CNO^- + 4OH^- = 2CO_2 + N_2 + 2H_2O + 6e$

Nothing, however, was mentioned regarding the isolation and verification of the products of the reactions ($NH_3$, $CO_2$, or $N_2$). The authors further reported that the decomposition of table salt during the electrolysis also leads to the oxidation of cyanide compounds by chlorine evolved at the anode:

$2Cl^- = Cl_2 + 2e$

$CN^- + Cl_2 + 2OH^- = CNO^- + 2Cl^- + H_2O$

$2CNO^- + 3Cl_2 + 4OH^- = 2CO_2 + N_2 + 6Cl^- + 2H_2O$

However, there was no evidence that chlorine gas is the oxidizing species. Nor was the actual role of chloride ion verified. Nowhere in the article could be found direct evidence supporting the proposed role of chloride ions in the reactions. Lately, Nagendran et al (15) electrolyzed aerated KCN solutions containing 500 ppm cyanide using graphite anodes and stainless steel cathodes. The solutions contained 10-70 g NaCl per liter. At a current density of 120 amp/$ft^2$, the cyanide concentration was reduced from 500 ppm to 0.5 ppm in 40 minutes; the energy requirement was 0.017 KWhr/g $CN^-$.

Recently, a claim for an electrochemical pollution control device was made which would treat dilute cyanide wastes at less than \$0.20/1b $CN^-$. This unit, using a bed of semi-conductive particles, was reported to be able to treat cyanide wastes at 300 GPH. At this time, the authors are unaware of the status of this treatment process (27).

Theoretical Considerations

In this section possible reaction mechanisms for the electrooxidation of $CN^-$ ion in the absence and presence of $Cl^-$, $Cl_2$ and $ClO^-$ are reviewed together with new experimental information obtained by the authors. The thrust of this discussion is to provide a theoretical basis for analyzing experimental results. This discussion does not purport to represent an exhaustive treatment of mechanism -- it is primarily concerned with constructing a framework upon which rational design of a demonstration unit can proceed.

The mechanism of the chemical oxidation or the electrochemical oxidation of $CN^-$ ion has never been fully elucidated. Little information on mechanism is available from the literature and most reports on electrooxidation of $CN^-$ ion generally only list energetically feasible thermal reactions and possible half-cell reactions (16). Cyanate, nitrogen, carbon dioxide, oxalate and ammonia have been mentioned as possible products of $CN^-$ ion oxidation and chlorine and hypochlorite as oxidation products of $Cl^-$ ion. In many reports reactions are presented with little comment on their validity as possible oxidation routes or on their significance to reactor design. Since the purpose of this report is to present a design of a demonstration unit for detoxication of dilute cyanide wastes, the authors undertook to study the electrochemical of cyanide using a differential flow reactor.

A differential reactor permits the evaluation of the effects of various reactor parameters which can be extended to the design of integral reactors (demonstration unit). A description of the differential reactor used in this study is given in Appendix A.

Electrooxidation of Cyanide Ion (Absence of Chloride): Electrooxidation of $CN^-$ ion in basic solution is generally represented by the following overall half-cell reactions ($\Delta F^o$ values calculated using data from Latimer (26)).

$$CN^- + 2OH^- = CNO^- + H_2O + 2e \qquad \Delta F^\circ = -44.79 \text{ kcal} \qquad [1]$$

$$CN^- + 4OH^- = CO_2 + \tfrac{1}{2} N_2 + 2H_2O + 5e \qquad [2]$$

The mechanisms of these reactions are not known.

It is probable that $CN^-$ ion is oxidized in an electrode surface reaction which chemisorbed oxygen or hydroxyl radical produced in the anodic discharge of hydroxyl ion. Reactions [1] and [2] can be described by the following reaction scheme.

$$2OH^- = 2OH + 2e \qquad \Delta F^\circ = -46.125 \text{ kcal} \qquad [3]$$

$$2OH = O + H_2O \qquad \Delta F^\circ = -19.756 \text{ kcal} \qquad [3a]$$

Overall reaction: $2OH^- = O + H_2O + 2e$ $\qquad \Delta F^\circ = -65.881$ kcal

$$CN^- + OH = CNO^- + H^+ + e \qquad \Delta F^\circ = -71.73 \text{ kcal} \qquad [4]$$

$$CN^- + O = CNO^- \qquad \Delta F^\circ = -118.194 \text{ kcal} \qquad [4a]$$

$$CN^- + 2OH = CO_2 + \tfrac{1}{2} N_2 + 2H^+ + 3e \qquad [5]$$

$$CN^- + O + H_2O = CO_2 + \tfrac{1}{2} N_2 + 2H^+ + 3e \qquad [5a]$$

The thermal reactions above are obviously energetically feasible. Further, since the applied voltage of an electrolysis cell can be adjusted at will, the anode potential can usually be made sufficiently positive to overcome the decomposition (activation) overvoltage of any cell reaction. From equation [1] or equations [4] and [5] it is obvious that pH will be an important reaction variable. Firstly, if $CN^-$ ion is the reactive species, the current efficiency would be expected to decrease markedly with decrease in pH of the anolyte -- due to protonation of $CN^-$ ion to form HCN. Conversely, at a high pH one would expect an increase in the surface coverage of the electrode by O and OH with a concomitant increase in the formation of molecular oxygen. Since combination of O to $O_2$ and of OH to $H_2O$ and $O_2$ are second order reactions, the increase in the rate of these reactions would be greater than the increase in the rates of the $CN^-$ ion oxidation reactions [4] and [5a] which are first order in O or OH.

In our investigation it was found that with cyanide solutions having a low concentration of buffer salts, the current efficiency in weakly basic solutions (9.5-10.5) was several times smaller than that obtained for solutions in pH range 12-12.3. In the presence of buffer salts (e.g., carbonates) the current

efficiency at pH ~ 12 was found to be only slightly higher than at pH ~ 10. A plausible explanation for these observations is as follows. Solutions with low concentrations of buffer salts have low buffer capacity at pH ~ 10. Discharge of hydroxyl ions would result in a decrease in the pH of the anolyte through hydroxyl ion polarization. And since $CN^-$ is a base ($pK_{HCN}$ = 9.32; 24, 25), the concentration of $CN^-$ would consequently decrease through protonation ($CN^- + H^+ = HCN$). Before electrolysis, the bulk pH is identical with the anolyte pH. However, during electrolysis, as hydroxyl ions are being discharged, a difference in pH between the anolyte and the bulk solution is established if the rate of hydroxyl ion consumption is faster than the hydroxyl ion flux (diffusion, transference) to the anolyte. Hence, the protonation of cyanide ion occurs. As this happens, the rates of reactions [4] and [5] would increase with increase in pH, that is, the hydroxyl polarization of the anode decreases with increasing pH. A similar argument explains the findings for solutions containing high buffer salt concentrations. Furthermore, this argument can be extended to partially explain the decrease in current efficiency with increasing current density.

Admittedly pH was thought by some investigators to have significance in the electrooxidation of cyanide. However, until now no reasonable explanation has been brought forward. The significance of pH changes, in the anolyte arising from hydroxyl ion polarization to the design of a demonstration unit, is clear.

Electrooxidation of $CN^-$ Ion in the Presence of Chloride: Data has accumulated which shows that chloride ion (added as NaCl, etc.) catalyzes or promotes the electrooxidation of cyanide. In our studies the chloride ion effect was examined and it was found that at pH ~ 10 there is a marked increase in current efficiency with increase in chloride/cyanide ratio. At pH ~ 12 the picture is quite different -- the presence of chloride has essentially no effect on current efficiency.

It is generally assumed that chloride effect is due to the presence of free hypochlorite (produced by electrooxidation of chloride ion) which oxidizes $CN^-$ ion by a thermal reaction. This may be valid in the electrolysis of concentrated brine-cyanide solutions. In the present case our studies show that chloride effect is not due to a bulk reaction but probably occurs as a result of an electrode surface reaction between electrochemically produced chemisorbed hypochlorite and $CN^-$ ion.

An explanation for the presence of a chloride ion effect at pH ~ 10 and its absence at pH ~ 12 is given below. The oxidation of $CN^-$ oxidation in the presence of $Cl^-$ will be a combination of the steps for $CN^-$ oxidation in the absence of $Cl^-$ together with the steps for reactions [8] and [9]. The proposed reaction scheme is given below.

(a) discharge of hydroxyl ions (surface reactions):

$$2OH^- = 2OH + 2e, \qquad \Delta F^o = -46.125 \text{ kcal} \qquad [3]$$

$$2OH = O + H_2O, \qquad \Delta F^o = -19.756 \text{ kcal} \qquad [3a]$$

$$O + O = O_2, \qquad \Delta F^o = -109.988 \text{ kcal} \qquad [6]$$

(b) $Cl^-$ oxidation (surface reactions):

$$Cl^- + OH = ClO^- + H^+ + e, \qquad \Delta F^o = 13.92 \text{ kcal} \qquad [7]$$

$$Cl^- + O = ClO^- \qquad \Delta F^o = -32.544 \text{ kcal} \qquad [7a]$$

(c) $CN^-$ oxidation:

surface reactions:

$$CN^- + OH = CNO^- + H^+ + e, \qquad \Delta F^o = -71.73 \text{ kcal} \qquad [4]$$

$$CN^- + O = CNO^-, \qquad \Delta F^o = -118.194 \text{ kcal} \qquad [4a]$$

$$CN^- + 2OH = CO_2 + \frac{1}{2} N_2 + 2H^+ + 3e \qquad [5]$$

$$CN^- + O + H_2O = CO_2 + \frac{1}{2} N_2 + 2H^+ + 3e \qquad [5a]$$

surface or bulk reactions:

$$CN^- + ClO^- = CNO^- + Cl^-, \qquad \Delta F^o = -85.65 \text{ kcal} \qquad [8]$$

$$2CN^- + 5ClO^- + H_2O \rightarrow 2CO_2 + N_2 + 5Cl^- + 2OH^- \qquad [9]$$

It is seen that in this reaction scheme, $Cl^-$ acts as a true catalyst, $Cl^-$ being regenerated in reactions [8] and [9]. The oxidation steps [7] and [7a] are similar to the $CN^-$ oxidation steps [4] and [4a] proposed in the previous section.

Considering the situation at pH $\sim$ 12, analysis of applied voltage data showed that there was no significant difference between estimated and experimental values over the $Cl^-/CN^-$ ratio 0 - 12. This is believed to reflect the absence of significant polarization at anode or cathode. Therefore, the constancy of current efficiency values over this range of $Cl^-/CN^-$ indicates that oxidation of $Cl^-$ by reactions [7] and [7a] must be slow relative to the oxidation of $CN^-$

by reactions [4] and [4a]. It might be argued that reactions [7] and [7a] are fast but that the $ClO^-$ produced does not react rapidly because reactions [8] and [9] are slow. This argument is refuted by the fact that reactor samples analyzed 24 hours after sampling showed no change in $CN^-$ concentration. Had residual $ClO^-$ been present, a change in $CN^-$ would have been observed.

A similar analysis on experimental and estimated applied voltage data at pH $\sim$ 10 shows large concentration over-voltages indicating significant hydroxyl ion polarization of the anode is present. Hydroxyl ion polarization of the anode would result in a decrease in $CN^-$ concentration in the anolyte through protonation, hence a decrease in the rates of reactions [5], [5a], [7] and [7a]. Thus one would not expect an increase (as observed) in current efficiency with increase in the $Cl^-/CN^-$ ratio. This may be explained by the presence of chloride ion, $Cl^-$ having provided an alternate route for $CN^-$ oxidation by reaction sequences [7], [7a], [8] and [9]. The result is an increase in the current efficiency of almost 100% for a $Cl^-/CN^-$ ratio of $\sim$ 6.

As anticipated the rates of reactions [7] and [7a] increased with increase in $Cl^-$ concentration. This is reflected by the higher current efficiency obtained when the $Cl^-/CN^-$ ratio was increased from 6 to 12. It should be pointed out that reactions [8] and [9] cannot simply be bulk solution reactions. Kinetic analysis of the oxidation of $CN^-$ by $ClO^-$ shows that, at the highest possible concentration of $ClO^-$ theoretically obtainable (by electrooxidation), the rate would be so slow that little cyanide would be oxidized in the reactor (residence time: 3.6 to 5.8 min). Therefore, reactions [8] and [9] must be catalyzed in some way and the most plausible explanation is that ClO produced in reactions [7] and [7a] is chemisorbed on the surface of the graphite anodes and that reactions [8] and [9] are anode surface reactions. One would expect a lowering of the activation energies for reactions [8] and [9] through chemisorption and this would be reflected in a higher reaction rate and hence, in higher values of current efficiency.

The above conclusions were obtained using a differential flow reactor. A similar chloride effect was observed in an integral reactor having bipolar electrodes.

Electrooxidation of $CN^-$ in the Presence of Some Plating Metals: In view of the fact that most cyanide wastes contain metals other than the alkali metals, an evaluation of the electrooxidation of cyanide solutions containing some common plating metals, e.g., zinc, cadmium and copper, was carried out. As mentioned previously, a differential flow reactor and bipolar integral reactors were used for this purpose.

In typical cyanide wastes (e.g., plating wastes), the cyanide is present not only as complexes of these metals but also in the free form. Assuming the metal complexes do not influence the electrooxidation of the free cyanide ion, one would expect the electrooxidation of the free cyanide in these solutions

would show little difference over simple cyanide solutions. This was in fact found with solutions containing cadmium and zinc. For example, there was little to distinguish between the electrooxidation of a 30 ppm NaCl solution and the electrooxidation of the free cyanide in a cadmium cyanide rinse solution containing 30 ppm free cyanide. However, it was observed that cyanide in the presence of Cu(I) is destroyed to a greater degree than corresponding solutions containing Cd(II). This copper effect was verified by testing copper containing cyanide solutions in the differential flow reactor. Cadmium cyanide solutions were also tested in this reactor. It was found that the presence of small amounts of Cu(I) sufficient to complex $\sim$ 10-30% of the total cyanide present resulted in some cases in the cyanide destruction being doubled. This copper effect was most significant in slightly basic solutions (pH $\sim$ 10-11). However, as will be noted in the following discussion on the operation of the demonstration unit, the presence of copper in test solutions did not apparently promote the electrooxidation of cyanide. Essentially the same current efficiency was obtained irrespective of the metals present.

## SECTION IV

## DEMONSTRATION UNIT

The purpose of this section is to describe the design, construction and operation of a demonstration unit for treating dilute cyanide plating wastes. The demonstration unit exploits the principle of bipolarization to charge an array of graphite electrode plates and cyanide wastes are electrolyzed in moving past the charged plates. A schematic of the demonstration unit and auxiliary equipment is shown in Fig. 1. A detailed description of the demonstration unit is given below.

Detail of Demonstration Unit: Fig. 2 shows the details of the demonstration unit. The unit consists of 1" AGSX graphite primary electrodes with interposed 35 1/8" AGSX graphite electrodes. The surface area of each of the electrodes is approximately 0.8 $ft^2$. The electrodes were drilled to permit a flow pattern as shown in the diagram. It was found that a flow pattern of this type was advantageous in promoting the expurgation of electrode gases. A centrifugal pump (PVC impeller) was used to provide a fluid velocity across the electrodes in the range of 0.8 to 1 ft/sec. At these velocities polarization of both the anodes and cathodes was reduced to a satisfactory low level. All piping and fittings were 1/2" schedule 40 PVC. A simple cloth filter was used to remove any suspended solids. A 0-150 V, 0-25 amp constant voltage-current power supply was used. The pH, conductivity, total and free cyanide, and heavy metals were monitored using standard techniques (17 - 23). All solutions were treated at room temperature.

Operational Modes: Cyanide wastes from electroplating operations can be treated in two modes - in a dragout duty mode and in a total kill mode. In a dragout duty mode the dragout load of the rinse tank is treated at a rate to maintain the cyanide concentration in the rinse tank within some predetermined range. In this mode the rinse water is conserved until the carbonate reaches an unacceptable level for satisfactory rinsing. When this point is reached the unit is transferred to the total kill mode. In the total kill mode the rinse water is cycled through the unit until the cyanide level is reduced to less than 1 ppm.

Operating Characteristics of the Demonstration Unit: All test solutions were recirculated through the demonstration unit at a rate of 3.7 U.S. gal./min in both the Dragout Duty and Total Kill Mode. The total volume of test solution was 13.1 U.S. gal. The data obtained for NaCN solutions, $Zn(CN)_2$ solutions and Cu/Zn cyanide solutions are shown in Figures 3a, 3b and 3c. These data are used below in the design calculations. Initial concentration of cyanide (total) were between 100 and 110 ppm. All solutions were 0.08 M in carbonate buffer - the pH was 9.8.

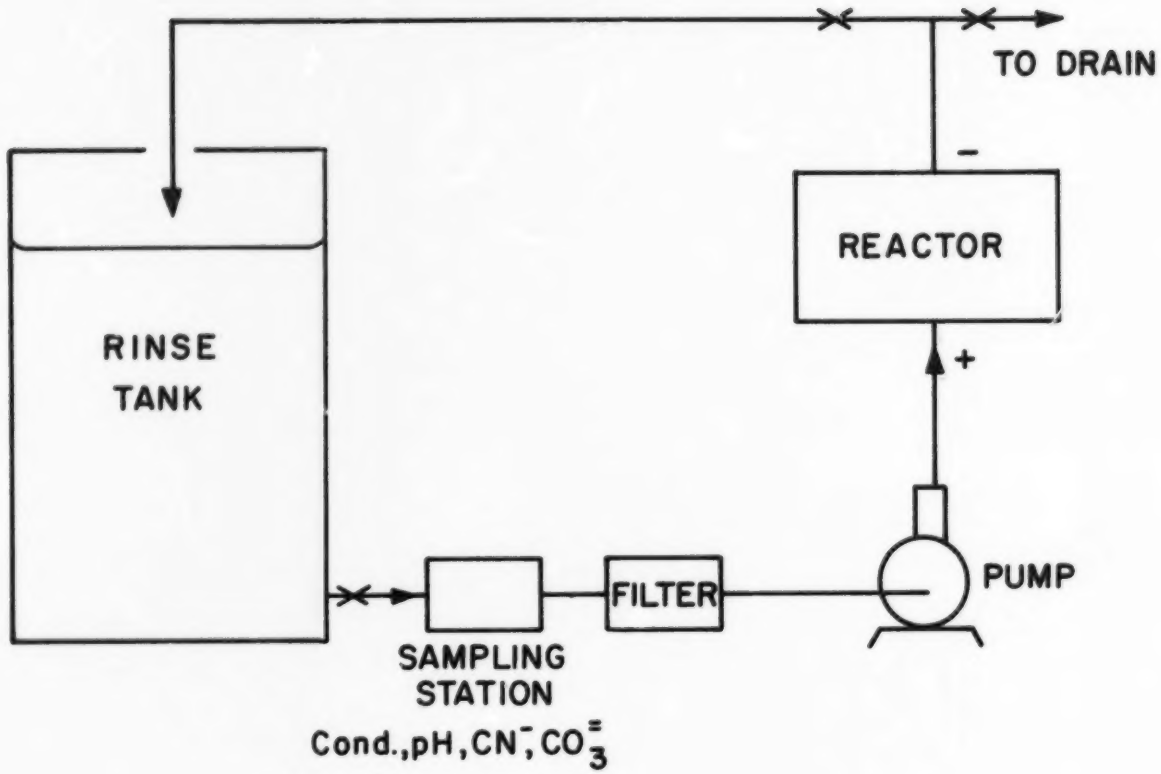


Fig. 1 SCHEMATIC DIAGRAM OF DEMONSTRATION UNIT AND AUXILIARY EQUIPMENT

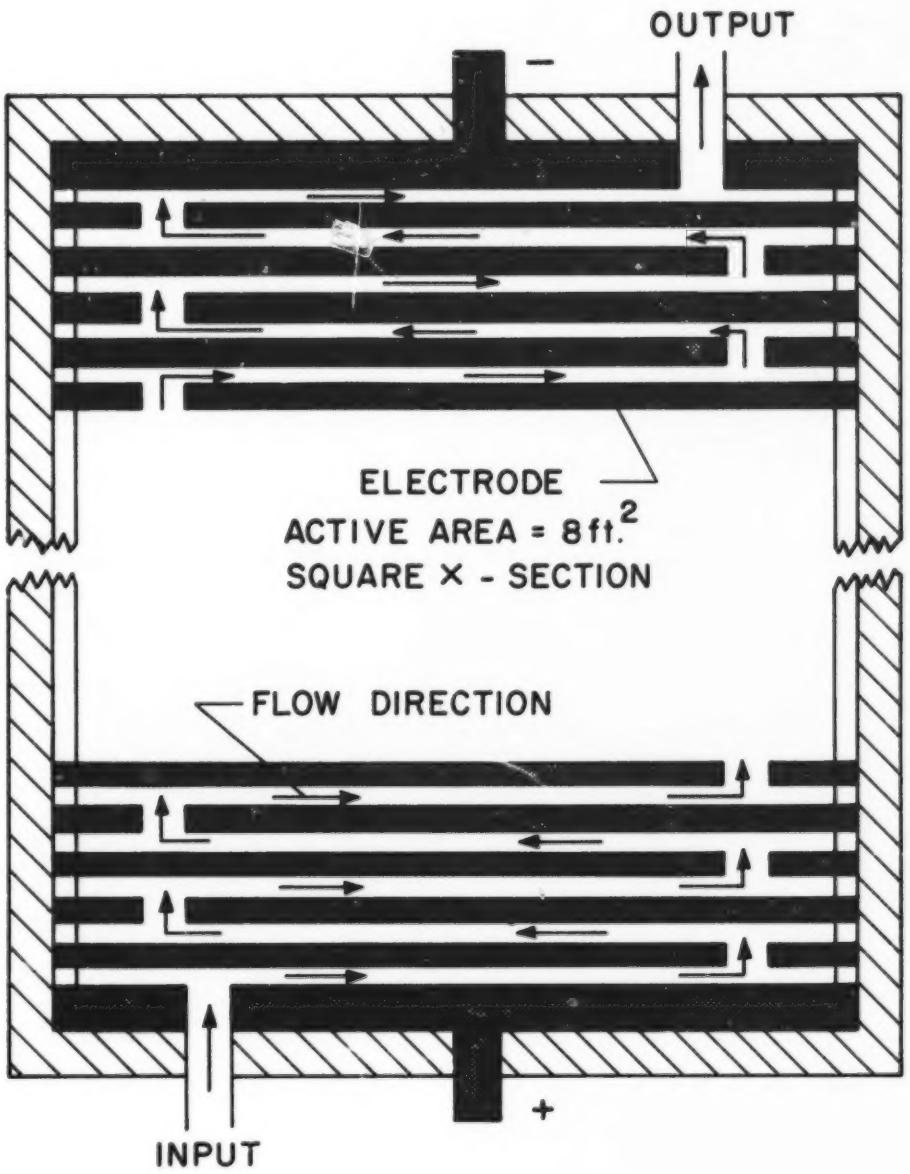


Fig. 2 DEMONSTRATION UNIT ( not to scale )

Process Design No. 1 : Treatment of NaCN Wastes

Dragout Duty Mode: This process design is for an electrooxidation reactor operating on a NaCN waste having an average steady-state concentration of $CN^-$ in the DDM of 50 ppm. The dragout duty was chosen as 4.8 lb $CN^-$/day. The reactor has been sized using $CN^-$ oxidation rate data from Figure 3a.

Data for Design:

$CN^-$ (free) = 50 ppm (steady-state value)

C.D. = 10 amp/$ft^2$

DD = 4.8 lb $CN^-$/day

Overdesign in DDM is 20%

Using these data and the process design equation in Appendix C, the operating Current $I_{op}$ is estimated to be 74.5 amp. Since the demonstration unit was operated at 8 amp (10 amp/$ft^2$), the reactor required would be equivalent to 74.5/8 demonstration units and would have a cross-sectional area of 7.45 $ft^2$. The energy requirement based on an applied voltage of 125 V (av.) is 46.6 KWhr/lb $CN^-$. The cost of treating the dragout of 4.8 lb $CN^-$/day at $0.01/KWhr is $2.24/day.

Total Kill Mode: This process design is for a $CN^-$ electrooxidation reactor operating in the Total Kill Mode on 1000 U.S.gal. of 50 ppm $CN^-$ (free) waste water. A final $CN^-$ level of 0.5 ppm was selected for the design. The rate data for $CN^-$ oxidation used in estimating the time required for the Total Kill step were obtained from Figure 3a.

Data for Design:

$CN^-$ (free, initial) = 50 ppm

$CN^-$ (free, final) = 0.5 ppm

C.D. = 10 amp/$ft^2$

A = 7.45 $ft^2$ (reactor cross-sectional area)

V = 1000 U.S. gal.

Using these data and the process design equations in Appendix C, the estimated time required to reduce $CN^-$ concentration from 50 ppm to 0.5 ppm is 5.25 hours. The energy requirement based on an average applied voltage of 120 V is 118 KWhr/lb $CN^-$. The cost of treating the 0.41 lb of $CN^-$ at $0.01/KWhr is $0.49.

Process Design No. 2 : Treatment of Roger's Brass Plating Rinsing Wasce

Dragout Duty Mode: In this process design the electrooxidation reactor will be sized to treat a dragout of 6 lb $CN^-$/day from a Roger's brass plating bath. For operation in the DDM, an average steady-state $CN^-$ (total) concentration of 100 ppm was chosen. The reactor has been sized using $CN^-$ oxidation rate data from Figure 3b.

Data for Design:

$CN^-$ (total) = 100 ppm (steady-state value)

C.D. = 10 amp/$ft^2$

DD = 6 lb $CN^-$/day

Overdesign in DDM is 10%

Using these data and the process design equations in Appendix C, the operating current $I_{op}$ is estimated to be 83.2 amp. This is equivalent to 83.2/8 demonstration units - the cross-sectional area of the reactor would be 8.32 $ft^2$. The energy requirement based on average applied voltage of 112 V is 37.3 KWhr/lb $CN^-$. The cost of treating the dragout of 6 lb $CN^-$/day at \$0.01/KWhr is \$2.24.

Total Kill Mode: This process design is for a $CN^-$ electrooxidation unit operating in the Total Kill Mode on 1200 U.S. gal. of 100 ppm (total) $CN^-$ rinsing waste. As in the previous design, a final (total) $CN^-$ concentration of 0.5 ppm was selected.

Data for Design:

$CN^-$ (total, initial) = 100 ppm

$CN^-$ (total, final) = 0.5 ppm

C.D. = 10 amp/$ft^2$

A = 8.32 $ft^2$ (reactor cross-sectional area)

V = 1200 U.S. gal.

Applying the process design equations (Appendix C) to these data and data from Figure 3b, the estimated time required to reduce the $CN^-$ concentration from 100 ppm to 0.5 ppm is 12.2 hours. The energy requirement based on an average applied voltage of 109 V is 116 KWhr/lb $CN^-$. The cost of treating the 0.96 lb of $CN^-$ at \$0.01/KWhr is \$1.12.

Process Design No. 3 : Treatment of Zinc (Cyanide) Plating Rinsing Waste

Dragout Duty Mode: In this process design the electrooxidation reactor will be sized to treat a dragout of 2.5 lb $CN^-$/day from a zinc (cyanide) plating bath. For operation in the DDM, an average steady-state $CN^-$ (total) concentration of 75 ppm was chosen. The reactor has been sized using $CN^-$ oxidation rate data from Figure 3c.

Data for Design:

$CN^-$ (total) = 75 ppm (steady-state value)

C.D. = 10 amp/$ft^2$

DD = 2.5 lb $CN^-$/day

Overdesign in DDM is 20%

Using these data and the process design equations in Appendix C, the operating current $I_{op}$ is estimated to be 35.2 amp. This is equivalent to 44.2/8 demonstration units - the cross-sectional area of the reactor would be 4.42 $ft^2$. The energy requirement based on average applied voltage of 114 V is 40 KWhr/lb $CN^-$. The cost of treating the dragout of 2.5 lb $CN^-$/day at \$0.01/KWhr is \$1.00.

Total Kill Mode: This process design is for a $CN^-$ electrooxidation unit operating in the Total Kill Mode on 600 U.S. gal. of 75 ppm (total) $CN^-$ rinsing waste. As in the previous design, a final (total) $CN^-$ concentration of 0.5 ppm was selected.

Data for Design:

$CN^-$ (total, initial) = 75 ppm

$CN^-$ (total, final) = 0.5 ppm

C.D. = 10 amp/$ft^2$

A = 4.42 $ft^2$ (reactor cross-sectional area)

V = 600 U.S. gal.

Applying the process design equations (Appendix C) to these data and data from Figure 3c, the estimated time required to reduce the $CN^-$ concentration from 75 ppm to 0.5 ppm is 10.1 hours. The energy requirement based on an average applied voltage of 110 V is 138 KWhr/lb $CN^-$. The cost of treating the 0.37 lb of $CN^-$ at \$0.01/KWhr is \$0.51.

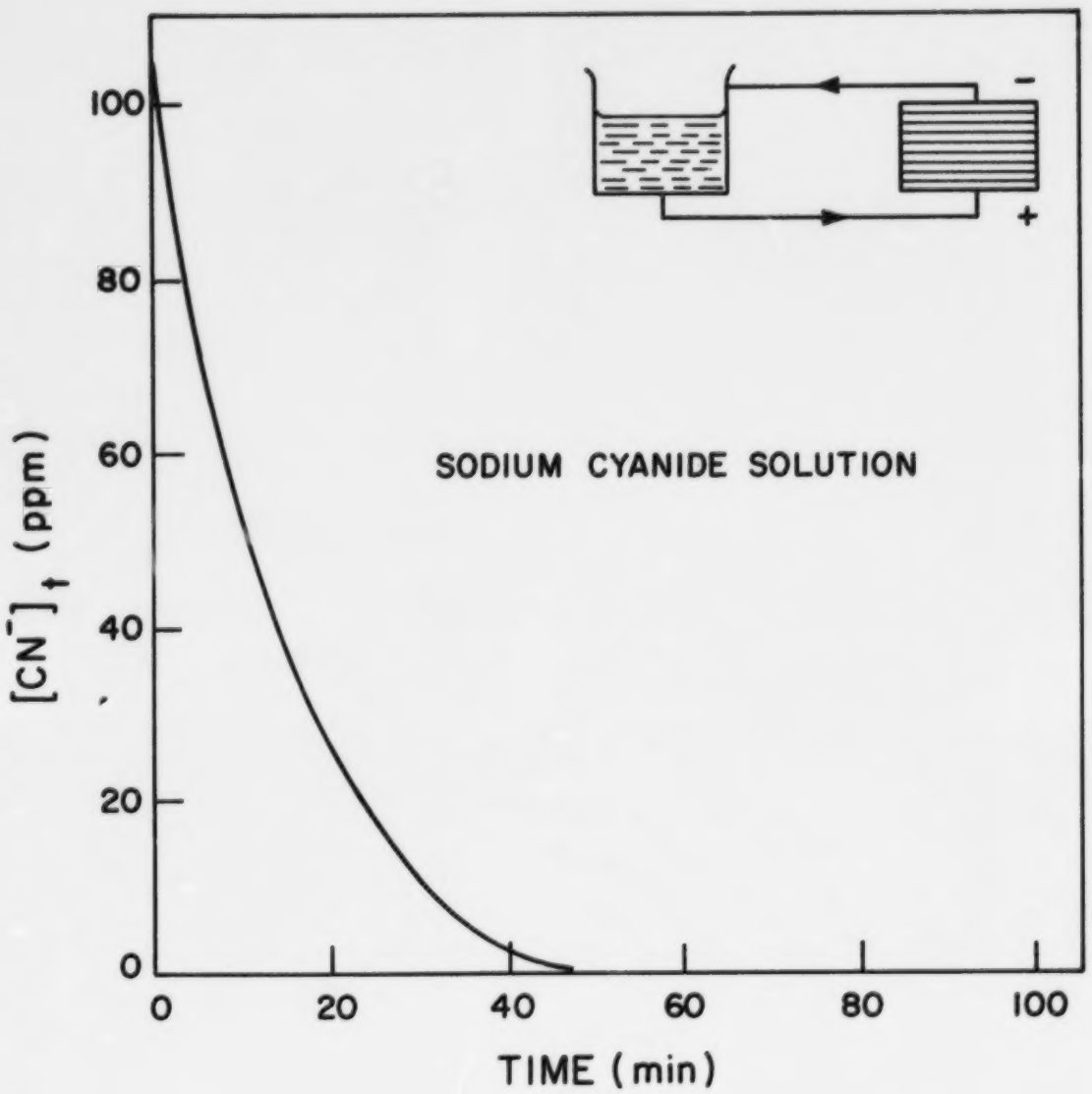


Fig. 3a AVERAGE OPERATING DATA FOR TREATMENT OF SODIUM CYANIDE SOLUTION

INITIAL $[CN^-]$ = 106 ppm

VOLUME OF SOLUTION = 13 U.S. gal.

$[CO_3^=]_t$ = 0.08 M

FLOW RATE = 3.7 U.S. gal. / min.

pH = 9.8

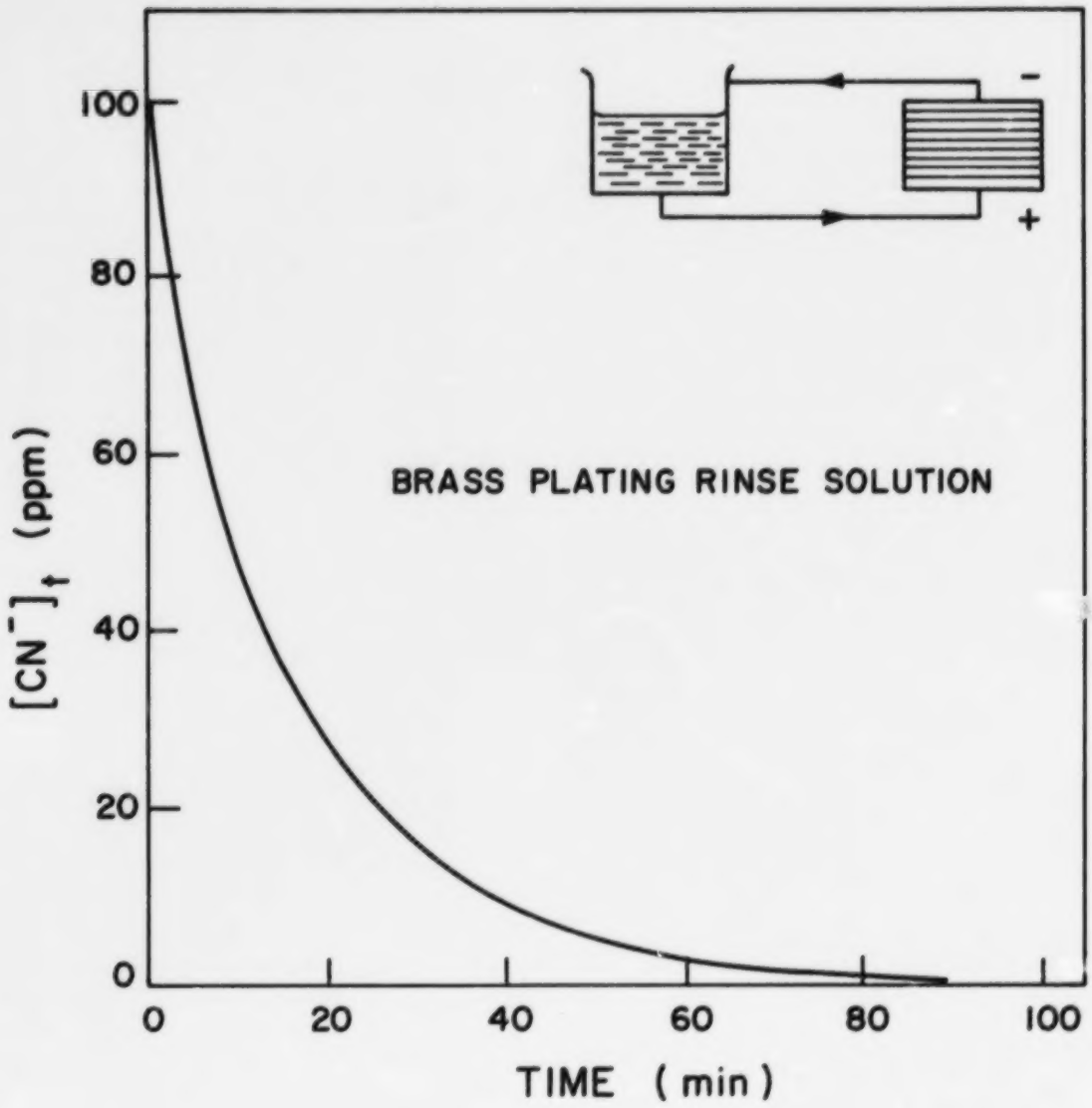


Fig. 3b AVERAGE OPERATING DATA FOR TREATMENT OF BRASS PLATING RINSE SOLUTION ( ROGER'S SOLUTION )

INITIAL $[CN^-]_t$ = 100 ppm

VOLUME OF SOLUTION = 13 U.S. gal.

$[CO_3^=]_t$ = 0.08 M

FLOW RATE = 3.7 U.S. gal. / min.

pH = 9.8

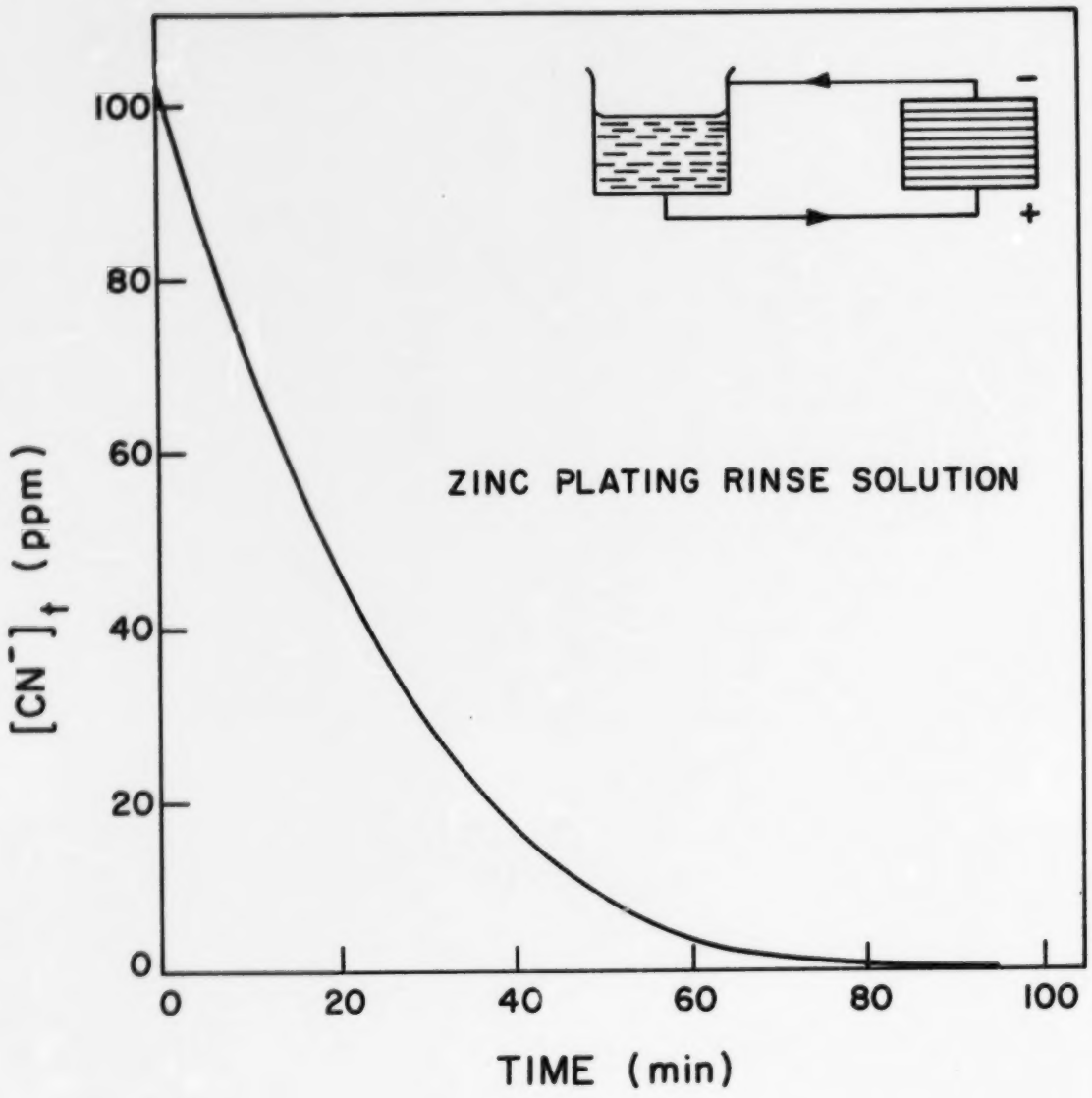


Fig. 3c AVERAGE OPERATING DATA FOR TREATMENT OF ZINC PLATING RINSE SOLUTION

INITIAL $[CN^-]_t$ = 102 ppm

VOLUME OF SOLUTION = 13 U.S. gal.

$[CO_3^=]_t$ = 0.08 M

FLOW RATE = 3.7 U.S. gal./min.

pH = 9.8

Combined Operation of the Dragout Duty Mode and the Total Kill Mode: Operating in the Dragout Duty Mode has the important advantage of conserving water. After a time, however, the buildup of carbonate salts makes the rinse water unsuitable because of carbonate blush or dragout, the point which this occurs depends, of course, on individual rinsing practice. When the rinse water must be disposed of, the electrooxidation reactor is transferred to the Total Kill Model to reduce $CN^-$ to less than 1 ppm.

Treatment of High Carbonate Cyanide Wastes: With a high dragout duty, the rate of accumulation of carbonate (from $CN^-$ oxidation) in the rinse water can be relatively rapid. And if carbonate blush is to be avoided, frequent changes of rinse water is necessary. To reduce the frequency of changes and thus conserve water, a secondary rinsing step might be used as backup for the primary rinse. Another important function of the secondary rinse is to accumulate the bulk of the cyanide dragged out from the first rinse tank. A schematic of the piping layout together with detailed operating instructions for a simple two tank static rinse system is given in Figure 4.

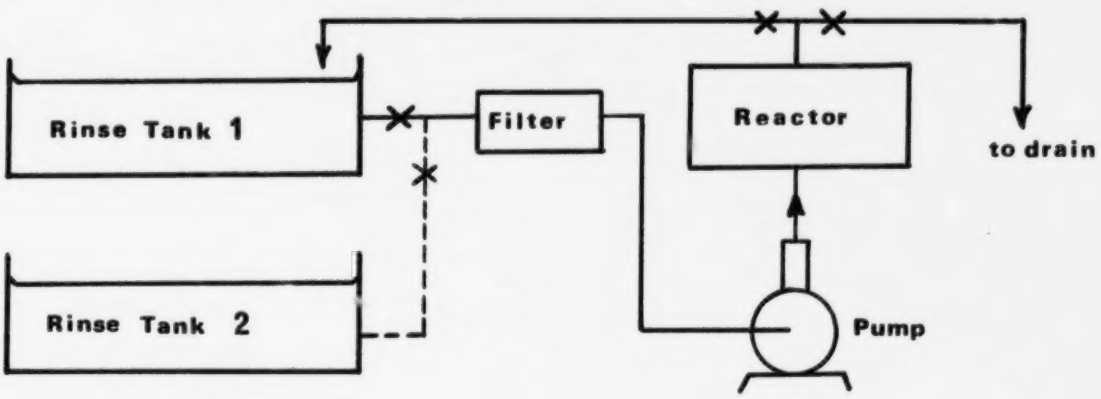


Figure 4 Schematic of a Two Rinse Tank Treatment System

Operation of System: (1) Operate rinse tank 1 without $CN^-$ treatment to allow $CN^-$ to buildup to the Dragout Duty Mode operating level. When this level is reached

(2) Switch the rinse tank 1 into the Dragout Duty Mode.

(3) During the Dragout Duty Mode of operation, an in-line cartridge filter collects any solids carried into the rinse tanks as well as $CaCO_3$ or $MgCO_3$ formed in situ. The filter also serves to remove solid $NaHCO_3$ and $Na_2CO_3$ formed after the rinse tank becomes saturated with respect to these salts. The purpose of the second rinse is to wash off the carbonate from the primary rinse thereby reducing carbonate blush.

(4) When the carbonate in the secondary rinse has reached an undesirable level, then the rinsing operation is stopped and the

primary rinse is treated in the Total Kill Mode to reduce the $CN^-$ to less than 1 ppm. This rinse water is pumped to the drain and the secondary rinse is pumped into the primary rinse tanks and fresh water is used for the secondary rinse. A schematic of the concentration changes in the rinse tanks is shown in Figure 5.

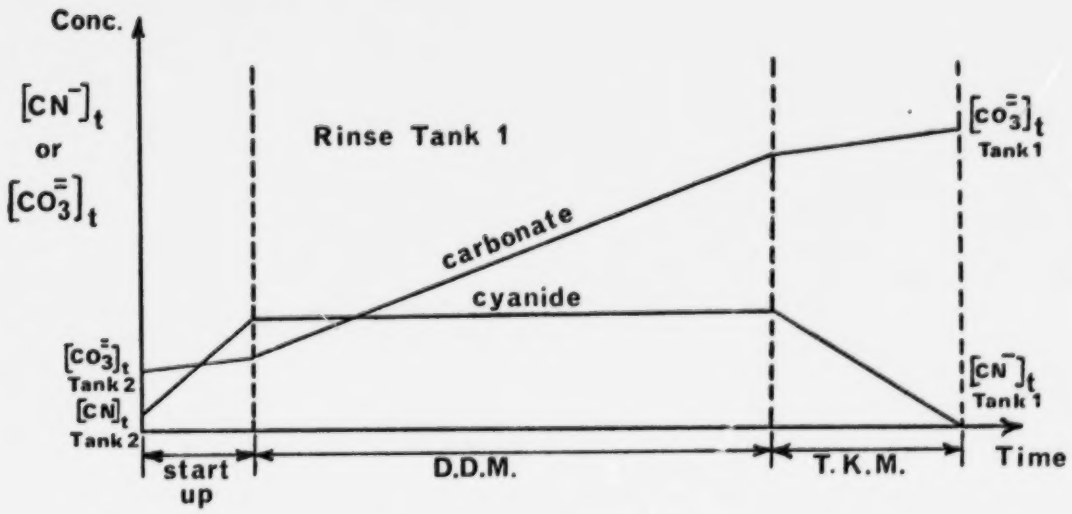


Figure 5 Schematic of the Concentration Profile of a Treatment System Operation with Two Rinse Tanks

## SECTION V

## DISCUSSION

The previous examples illustrate the approach to reactor sizing. The first step is to size the reactor on the basis of the dragout duty and establish the time the reactor will be operated in the Dragout Duty Mode. This time will depend, of course, on the level of carbonate salts that can be tolerated in the rinse bath. The next step is to calculate the time required for the Total Kill Mode and the ratio (time in TKM)/(time in DDM). Since time in the Total Kill Mode represents a down-time for the rinse bath, the value of this ratio should be small, e.g., in the region of 0.1 or less.

It should be noted that in designing the process, the highest steady-state $CN^-$ concentration that can be tolerated should be used in the Dragout Duty Mode. The reason for this is that the overall specific energy requirement depends primarily on the specific energy requirement in the Dragout Duty Mode - the higher the operating level of $CN^-$, the lower the specific energy requirement. Our example will make this clear. In the reactor design (p. 18) for treating Roger's brass plating rinse water, the specific energy requirement for the Dragout Duty Mode operating at 100 ppm $CN^-$ (total) is 37.3 KWhr/lb $CN^-$; in the Total Kill Mode it is 116 KWhr/lb $CN^-$. Choosing a reasonable operating cycle of 5½ days (5 days in DDM, ½ day in TKM), the overall specific energy requirement is 39.7 KWhr/lb $CN^-$. This can be contrasted with a design for the same dragout duty (6 lb $CN^-$/day) in which the $CN^-$ operating level in the Dragout Duty Mode was chosen at 25 ppm $CN^-$ (total). The reactor required is about 3 times as large and the specific energy requirement in the Dragout Duty Mode and in the Total Kill Mode are respectively $\sim$ 110 and $\sim$ 380 KWhr/lb $CN^-$. The overall specific energy requirement for a corresponding 5½ day cycle is $\sim$ 112 KWhr/lb $CN^-$. Thus, the penalty for operating the Dragout Duty Mode at 25 ppm instead of 100 ppm $CN^-$ is a three-fold increase in the reactor size and in the energy requirement.

The operational data for the Demonstration Unit shown in Figures 3(a)(b)(c) were obtained with cyanide solutions buffered at pH $\sim$ 9.8 with $\sim$ 0.08 M carbonate buffer. The carbonate salts not only provided buffer capacity but also served to make the solution more conducting. From the standpoint of process design, the adjustment of pH, buffer capacity and conductivity of fresh rinse baths is desirable. This can be done most simply by treating fresh rinse with an appropriate amount of carbonate-rich water from the preceding rinse cycle. Common salt may also be used to raise the conductivity of the bath. Salt should not, however, be considered a substitute for carbonate - the promotive effect of $Cl^-$ on $CN^-$ oxidation cannot offset the decrease in the efficiency of $CN^-$ oxidation that arises when strong hydroxyl polarization of the anode occurs. The problem of insufficient buffer capacity disappears, of course, as time goes on since carbonate is a product of $CN^-$ oxidation. Further, as carbonate salts build up, the power requirement decreases due to a decrease in the applied voltage.

During electrochemical treatment of cyanide wastes, plating metals are electrodeposited on cathodic surfaces. From time to time stripping of these deposits is necessary. If down-time is not critical, the deposits can be stripped mechanically - this, of course, involves dissassembly of the reactor. Alternatively the deposits can be acid leached and metal values recovered as hydroxides or carbonates for reuse in plating bath makeup. If the composition of the deposits is compatible with a cyanide plating bath, a cyanide leach using cyanide plating solutions is the preferred method.

Recirculation of cyanide waste through the reactor serves two main purposes: first, the shearing action of the solution effectively cleans the electrode surfaces of gases produced electrochemically. Secondly, cyanide polarization of the anodes is significantly reduced by the constant renewal of solution in the anolyte. Experience with the Demonstration Unit has shown that a fluid velocity between electrode plates of $\sim$ 1 ft/sec for every 10 amp/ft$^2$ is sufficient for these purposes. The following relation may be used to estimate the recirculation rate:

$$Q = 449\ v\ \frac{A}{\ell} \cdot g \cdot (I^*/10\ \text{amps/ft}^2)$$

where Q is the U. S. gal/min

v is the flow velocity across the electrodes in ft/sec

A is the reactor cross-sectional area in ft$^2$

$\ell$ is the length of the electrode in the direction of flow in ft

g is the electrode gap in ft

I* is the current density in amp/ft$^2$

449 is from the conversion of ft$^3$/sec to gal/min

10 amps/ft$^2$ was found experimentally for a fluid velocity between the electrode plates of $\sim$ 1 ft/sec

In general, electrochemical reactions exhibit relatively high activation energies, and therefore, operation of the electrooxidation reactor will show an increased efficiency as the rinse bath temperature is increased. In this report the operational data for the demonstration unit was obtained at room temperature (25-30$^o$C). And since the reactor design examples were based on the operational data in Figures 3a,b,c, the designs represent a conservative estimate of the reactor size required for the given dragout duties.

## SECTION VI

## CAPITAL COSTS

Capital cost provided below is for the reactor system described in Process Design No. 2 (Treatment of Roger's Brass Plating Rinsing Waste) in which the reactor has 8.32 $ft^2$ cross-sectional area with 35 electrodes.

| | | |
|---|---|---|
| Reactor Core | $ 2,500 | (1) |
| D.C. Power Supply (constant current type) | 2,600 | |
| Pumps, piping | 800 | (2) |
| In-line cartridge type filter | 200 | |
| Monitoring and control | 2,800 | (3) |
| Holding tank (1500 gal.) | 800 | |
| Installation | (500) | (4) |
| | $10,200 | (5) |

The capital cost estimate is based on early 1973 field information. It is believed to be reasonable (± 10%) for a $CN^-$ treatment system designed for in situ treatment in a 1200 gal. rinse bath at a rate of 6 lb $CN^-$/day at a nominal steady state level of 100 ppm. The estimate for monitoring and controls is for an automatic control system (using a conductivity sensor) for cycling the reactor between DDM and TKM operation.

Comments

(1) Based on the authors estimate of scaling up from the Demonstration Unit
(2) This figure could be reduced by ~ $600 if an existing pump could be adapted for use for the reactor
(3) If manual operation was adopted this figure might be reduced by ~ $1500-2000
(4) This item covers ~ 30 hours of plumbing/electrical work. It does not include millright work which most users could handle themselves
(5) Not included is the equipment cost for automatic adjustment of pH of treated wastes. Since the TKM operation might be carried out only once a week or once every two weeks, manual pH adjustment/check would not significantly increase operating cost.

## SECTION VII

## ACKNOWLEDGMENTS

The assistance of Mr. Klaus Oehr and Mr. Rolland Gaillard who carried out much of the experimental work is acknowledged and the co-operation during the project of the Department of Chemical Engineering of the University of Waterloo is gratefully acknowledged.

The support of the project by the Environmental Protection Agency and the help provided by Mr. William J. Lacy, Mr. Edward L. Dulaney and Mr. Clifford Risley, Jr., Project Officer, is acknowledged with sincere thanks.

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## SECTION IX

## GLOSSARY

| | |
|---|---|
| g/l | grams per litre |
| M | molar or moles per litre |
| N | normality, concentration in equivalents/litre |
| U.S. gal. | United States gallon |
| U.S. gal./min | United States gallons per minute |
| U.S. gal./hr | United States gallons per hour |
| ppm | parts per million or mg/litre |
| $[CN^-]_t$ | total cyanide concentration |
| $[CN^-]$ | free cyanide concentration |
| $[CO_3^=]_t$ | total carbonate concentration |
| pH | (-log)of hydrogen ion concentration |
| pK | (-log)of equilibrium or stability constant |
| $\Delta F^o$ | standard free energy of formation |
| KWhr | killowatt-hour |
| KWhr/lb | killowatt-hour per pound |
| KWhr/g | killowatt-hour per gram |
| C.D. | current density |
| C.E. | current efficiency |
| DDM | dragout duty mode |
| TKM | total kill mode |
| AGSX | Union Carbide Corporation designation for resin free electrode graphite |
| PVC | Polyvinyl chloride |
| CSTR | Continuous stirred tank reactor |
| DD | dragout duty(in lb$CN^-$ / day) |
| t* | time for total kill(in hours) |

## SECTION X

## APPENDICES


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## Appendix A

Electrochemical Apparatus used in the Fundamental Study of the Cyanide Electrochemical Process

Annular Flow Reactor (Differential Type):

The annular flow reactor shown in Fig. A-1 was of the downflow type consisting of a graphite pipe as anode and a central graphite rod as cathode. The anode was fabricated from a 4-inch graphite cylinder which was bored out to 3 inches. Graphite rods served as cathodes. The effective length of the electrolysis section of the reactor was 10 inches. Electrical contacts for anode and cathode were provided by clamping copper sheets around the electrodes as shown in Figure A-1.

This reactor is of the differential type -- that is, it is designed purposely to operate at low conversions. By operating at low conversions the conditions along path of flow are not appreciably different, hence the data from the reactor can be analyzed on the basis of average conditions in the reactor. This type of operation considerably simplifies analysis of data, yet preserves the condition that the data is obtained under flow conditions.

A schematic diagram of the electrolysis apparatus is shown in Figure A-2. Cyanide test solution, prepared in the mixing tank, was pumped by air pressure into two storage tanks. A constant-head gravity flow system fed the cyanide test solution downwards through a glass-tubing coil (10 turns) immersed in a constant-temperature water bath maintained within $\pm$ 0.2°C of the desired temperature, to the annular flow reactor. A constant flow rate was obtained by adjusting a control valve at the discharge end of the reactor to the desired rate of flow. A Hewlett-Packard constant voltage/constant current d.c. power supply (Harrison Laboratories, Model 6266A) was used for electrolysis. An auxiliary voltmeter and ammeter (Nichols, Model 605 Moving Coil) were used for accurate measurement of the current and applied voltage.

Other Reactors used in the Fundamental Study:

Although most of the fundamental study was carried out with the Annular (differential) Flow Reactor, tests using small integral reactors also proved useful. The integral reactors were of three types. The first was a simple two litre batch reactor which was used mainly for qualitative work - e.g., observing surface density of gassing, electrode erosion and degree of preferential deposition vertically and transversely across the graphite electrodes. The other reactors were of the flow type and were used mainly in studying the behavior of bipolar electrode systems. One reactor was of the quasi plug-flow type having a series of vertical, closely spaced, 1/8" thick graphite bipolar electrodes interposed between 1" thick primary graphite electrodes. The electrodes were drilled at alternate edges to permit horizontal switch-back flow past the bipoles. In some

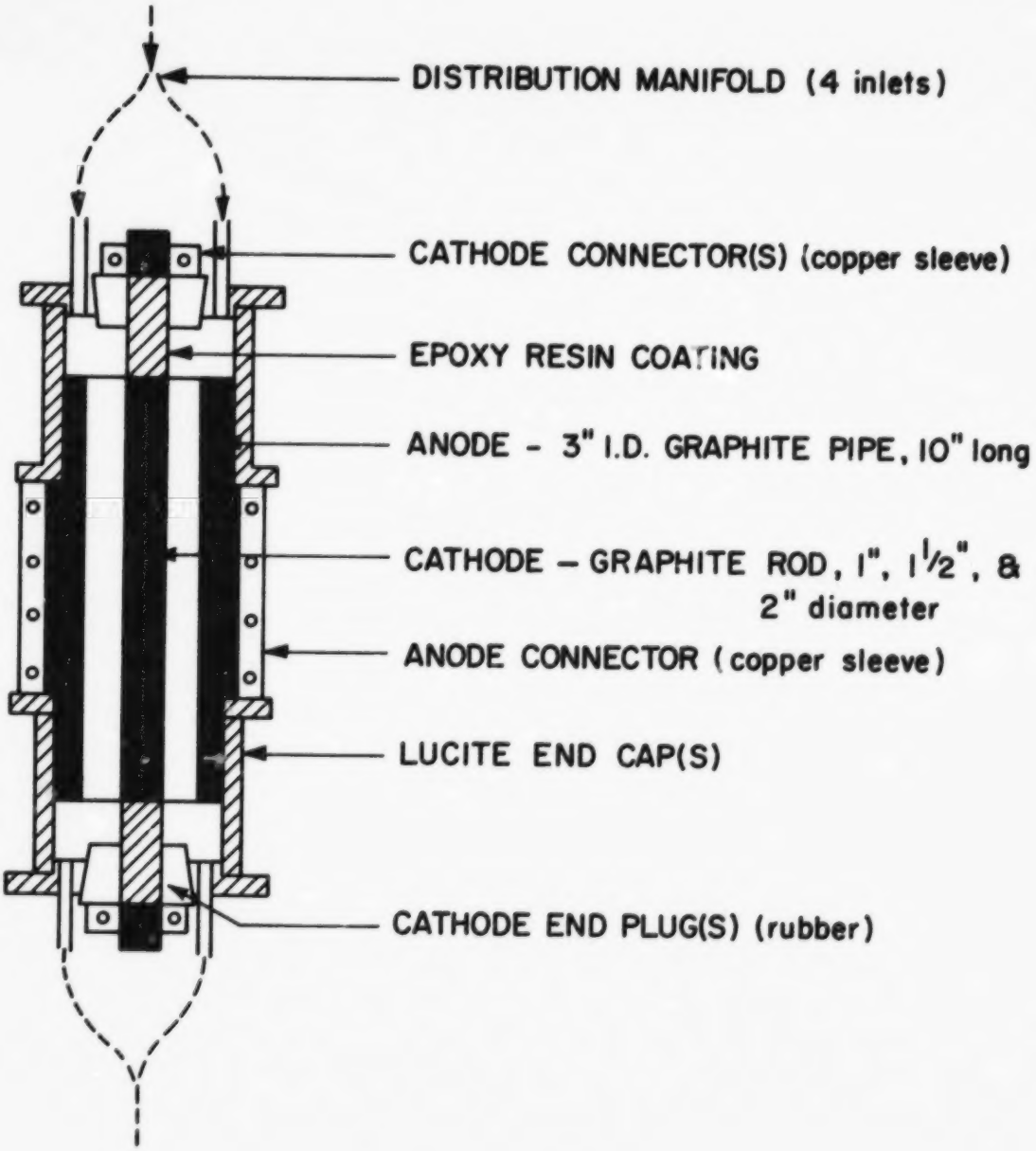
DISTRIBUTION MANIFOLD (4 inlets)
CATHODE CONNECTOR(S) (copper sleeve)
EPOXY RESIN COATING
ANODE - 3" I.D. GRAPHITE PIPE, 10" long
CATHODE – GRAPHITE ROD, 1", 1½", & 2" diameter
ANODE CONNECTOR (copper sleeve)
LUCITE END CAP(S)
CATHODE END PLUG(S) (rubber)

Fig. A-1 ANNULAR FLOW REACTOR FOR ELECTROLYZING AQUEOUS $CN^-$ SOLUTION
(¼ actual size)

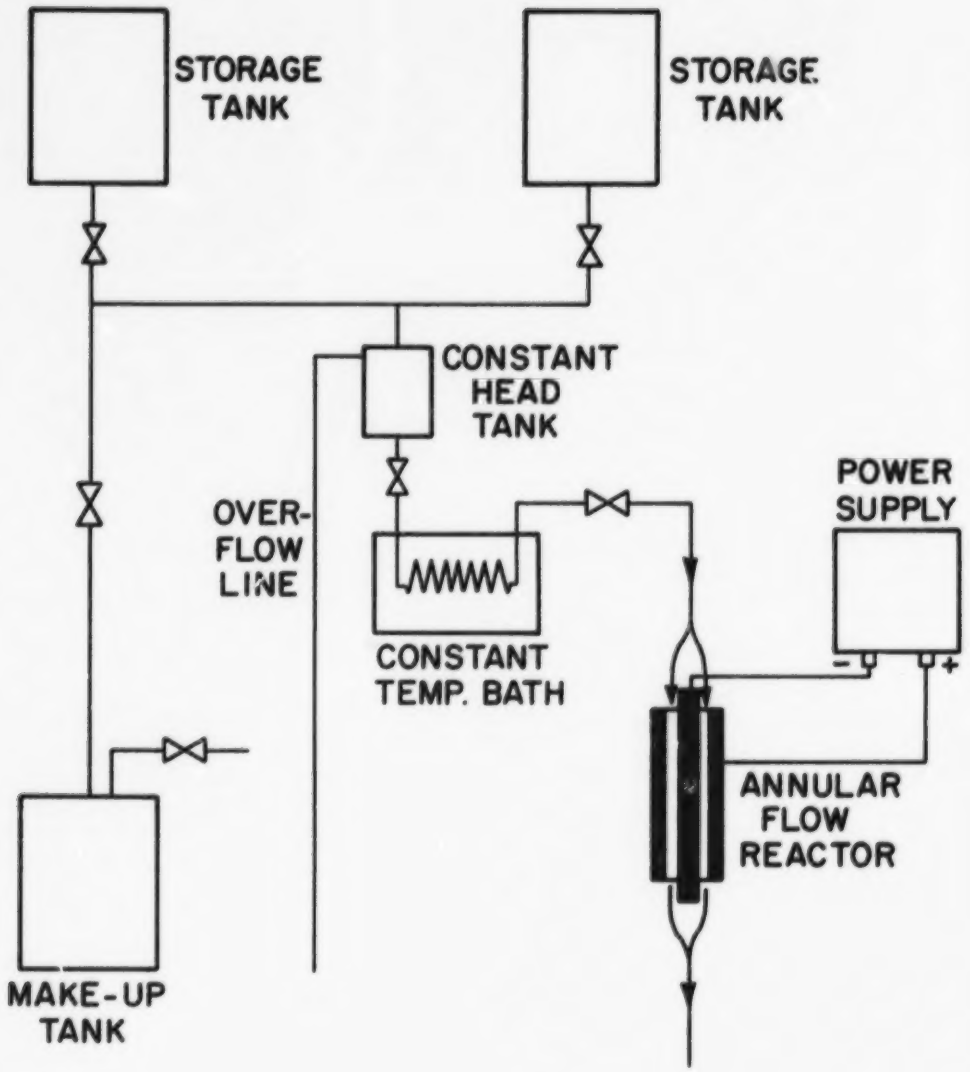


Fig. A-2 A SCHEMATIC DIAGRAM OF THE ELECTROLYSIS APPARATUS

experiments plate bipoles were replaced by flow-through bipolar electrodes consisting of a grid of 3/16" graphite rods. A CSTR type flow reactor was also used for testing electrooxidation efficiency.

Some work was carried out using a fluidized bed of graphite particles. The purpose was to study the degree of electrooxidation of $CN^-$ at particulate bipoles. This line of investigation was felt not to be fruitful due to the inability of maintaining a uniformly fluidized bed at even moderate current densities.

## Appendix B

Determination of Cyanide:

The determination of cyanide was carried out titrimetrically using 0.01N $AgNO_3$ solution and t-(p-(dimethylamino)benzylidine) rhodanine as indicator (18-23). Duplicate samples, each 100 ml aliquots, of sodium cyanide solution were used during the analysis. Before titration, the pH was adjusted to 11 - 12 using 2% NaOH solutions.

The $AgNO_3$ method (modified Liebig Titration) for determining cyanide was carefully checked using a standard NaCN solution obtained from British Drug Houses. Solutions containing cyanide ion in the range 10 - 50 ppm were analyzed in the presence and absence of chloride ions under various conditions of dilution, pH and indicator concentration. Initial determinations gave an average deviation of about $\pm$ 2.5% but after experience was gained, average deviations of less than 1.5% were obtained without difficulty with cyanide at the 10 ppm level.

The feasibility of using silver or platinum electrodes for continuously monitoring cyanide ion was investigated but reproducible results were not obtained. The use of a commercial cyanide electrode for analyzing free $CN^-$ ion was considered. After extensive testing it was found that the electrodes (2 were tested) were too unstable to be of any practical use in our work. A new redesigned electrode has been submitted for our evaluation. Initial tests indicate no significant improvement -- Nernst response seldom obtains and drifts of 3-5 millivolts over a period of only 2-3 hours is common.

## Appendix C

Process Design Equations based on Operating Characteristics of the Demonstration Unit

Design Equations for the Dragout Duty Mode:

(a) The theoretical operating current $I_{th}$ required in the Dragout Duty Mode to treat cyanide at a Dragout Duty of DD lb $CN^-$/day at a steady-state level (av.) of C ppm is given by

$$I_{th} \text{ (ampere)} = 50.5 \text{ DD} \left[ \frac{\Delta CN}{\Delta t} \right]^{-1}$$

where $\left[ \frac{\Delta CN}{\Delta t} \right]$ is the slope of the Demonstration Unit operating curve in ppm/min at a cyanide concentration of C ppm.

(b) The practical operating current $I_{op}$ calculated on the basis of x% over-design is given by

$$I_{op} \text{ (ampere)} = \left( \frac{100+x}{100} \right) I_{th}$$

(c) The cross-sectional area A of a reactor operating at $I_{op}$ ampere at a current density of 10 amp/$ft^2$ is given by

$$A \ (ft^2) = 0.1 \ I_{op}$$

(d) The solution recirculation rate required for a reactor of cross-sectional area A operating at 10 amp/$ft^2$ may be estimated by

$$Q \text{ (U.S. gal./min)} = 449 \ v \frac{A}{\ell} \ g \ (I^*/10)$$

where Q is in U.S. gal./min, v is the flow velocity in the reactor, A is the cross-sectional area of the reactor in $ft^2$, $\ell$ is the length of an electrode in the direction of flow in ft, g is the electrode gap in ft and I* is the current density in amp/$ft^2$, 10 is the current density found for a fluid velocity of $\sim$1 ft/sec between electrode plates, and the factor 449 is from the conversion from $ft^3$/sec to gal/min.

(e) Energy requirement expressed as KWhr/day and KWhr/lb $CN^-$ are given by

(i) $$ER/D \text{ (KWhr/day)} = 0.024 \text{ v } I_{op}$$

(ii) $$ER/P \text{ (KWhr/lb } CN^-) = \frac{0.024 \text{ v } I_{op}}{DD}$$

where v is the applied voltage of the reactor.

Design Equations for the Total Kill Mode:

(a) The treatment time, t* hours, required to reduce the concentration of cyanide in V gal. of solution from $C_i$ ppm to $C_f$ ppm with a reactor of A $ft^2$ cross-sectional area operating at 10 amp/$ft^2$ is given by

$$t^* \text{ (hours)} = \frac{0.001 \text{ V } (t_i - t_f)}{A}$$

where $t_i$ and $t_f$ are the times in minutes corresponding to cyanide concentrations $C_i$ and $C_f$ on Figures 3(a), 3(b) and 3(c).

(b) Energy requirements expressed KWhr and KWhr/lb $CN^-$ are given by

(i) $$ER(TKM) \text{ (KWhr)} = 0.001 \text{ t* v } I_{op}$$

(ii) $$ER/P \text{ (KWhr/lb } CN^-) = 120 \frac{t^* \text{ v } I_{op}}{V (C_i - C_f)}$$

(c) The solution recirculation rate may be estimated using the expression given above for the Dragout Duty Mode of operation.